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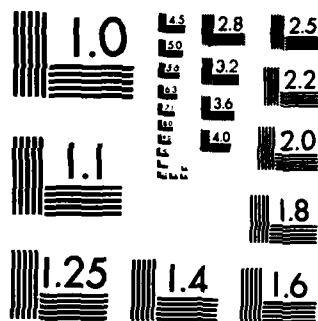
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Polyphosphazene Solid Electrolytes



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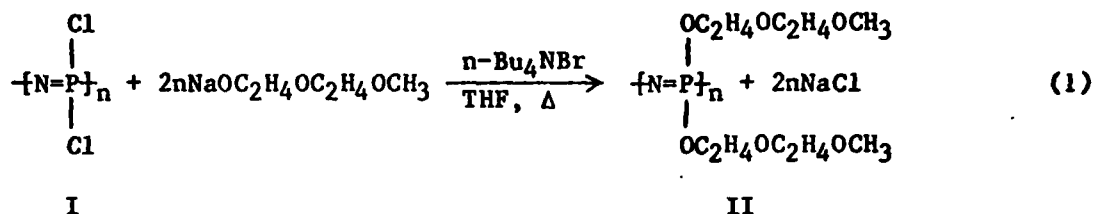
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Considerable attention is currently focused on inorganic ion conducting solids^{1,2} from both a fundamental standpoint and for their use as electrolytes in high energy density batteries and sensors. Recently, a radically new battery design based on a solvent-free thin film polymer electrolyte, has been tested and found promising for medium temperature (ca. 100°C) applications.³ In the present communication we report a new type of host polymer which forms complexes with a wide variety of metal salts having good conductivity at room temperature. The dependence of conductivity on salt concentration shows a distinct maximum which is consistent with current theory of charge transport in these materials.

Research on the ion transport in polymer-salt complexes electrolytes implicates a liquid-like mechanism.⁴ One criterion for the requisite polymer fluidity is a low glass transition temperature, T_g .^{4,5} This consideration prompted us to explore salt complexes of polyphosphazenes, because some polyphosphazenes exhibit very low glass transition temperatures,⁶ and the extensive chemistry of poly(dichlorophosphazene), $[\text{NPCl}_2]_n$, affords the opportunity for easy modification.

The sodium salt of 2-(2-methoxyethoxy)ethanol was allowed to react with poly(dichlorophosphazene) (I) in the presence of tetra-*n*-butylammonium bromide⁷ to yield the fully substituted, stable high polymer MEEP (II) (eq. 1).



³¹P, ¹³C NMR and elemental analysis all indicate total halogen replacement has occurred.⁸

Solvent-free complexes were prepared by vacuum removal of THF from solution containing a predetermined ratio of polymer and salt. All complexes were found to be amorphous by x-ray diffraction, optical microscopy, and differential scanning calorimetry (DSC). The complexes range from a hard material at 2:1, metal cation:polymer repeat unit, concentration to a rubbery, elastic species at 0.25:1 and lower stoichiometries and a corresponding increase in the glass transition temperature, *T_g*, was observed.

Conductivities were measured with a vector impedance meter and analyzed by complex impedance techniques between 5 to 500,000 Hz.⁹⁻¹¹ Polarization cell experiments indicate that the transference number for Ag⁺ is 0.03 or less at 50°C and for Li⁺ it is 0.32 under the same conditions. Gentle curves are obtained, when the conductivity data are plotted as either $\ln(\sigma T^{1/2})$ or $\ln \sigma$ vs $1/T$, Figure 1, as expected for amorphous polymer electrolytes.^{4,12,13}

Insert Figure 1 Here

The conductivity of a polymer electrolyte, as given by a configuration entropy model, follows equation 2, where the A term is proportional to the number of charge carriers and the T_0 term, in the exponential, is closely related to the glass transition of the sample.^{4,13}

$$\sigma = AT^{-1/2}\exp(-B/(T-T_0)) \quad (2)$$

The conductivity of $(\text{AgSO}_3\text{CF}_3)_x \cdot \text{MEEP}$ complexes increased with increasing salt concentration as expected ($0 < x < 0.17$), however, further increases in salt concentration resulted in diminished conductivities, Figure 2. The progressive immobilization of polymer chains resulting in restricted segmental motion of the polymer and increased rigidity would account for the rising T_g values and decreasing conductivities observed.¹²⁻¹⁴

Insert Figure 2 Here

Complexes of poly(ethylene oxide), and LiSO_3CF_3 or LiClO_4 (0.125:1), are useful battery electrolytes above 100°C .¹⁵⁻¹⁷ Between room temperature and 100°C , the conductivity of $(\text{LiSO}_3\text{CF}_3)_{0.25} \cdot \text{MEEP}$ is between 1-3 orders of magnitude larger than that of the poly(ethylene oxide) systems. Thus in contrast with the polyether-based electrolytes the new polyphosphazene electrolyte is a good candidate for a room-temperature thin-film battery. Concentration dependence of the ion mobility and T_g for the new phosphazene electrolytes substantiate current models for the influence of charge carrier concentration and fluidity on the ion transport in solvent-free polymer-salt complexes.

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References and Footnotes:

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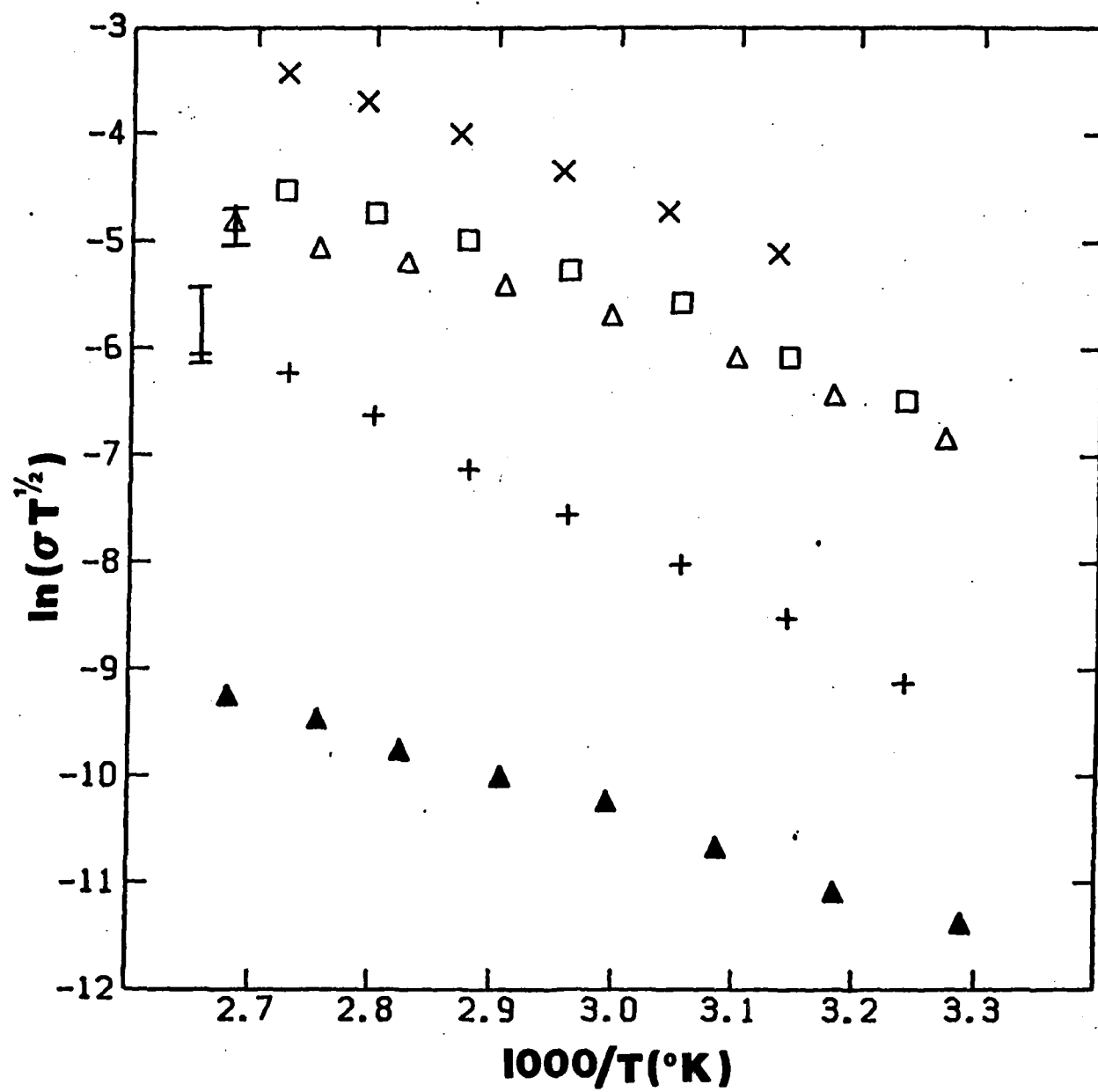
- (1) Yao, Y. Y.; Kummer, J. T. J. Inorg. Nucl. Chem. 1967, 29, 2453.
- (2) Farrington, G. C.; Briant, J. L. Science 1979, 204, 1371.
- (3) Sequeira, C. A. C.; Hooper, A. Extended Abstracts, 163rd Meeting Electrochemical Society 1983, 83, 751, Abstract No. 493.
- (4) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. in "Fast Ion Transport in Solids": Vashista, P.; Mundy, J. N.; Shennoy, G. D. eds., North-Holland: New York, 1979, 131-136.
- (5) (a) Papke, B. L.; Ratner, M. A.; Shriver, D. F. J. Phys. Chem. Solids 1981, 42, 493.
(b) Papke, B. L.; Dupon, R.; Ratner, M. A.; Shriver, D. F. Solid State Ionics 1981, 5, 685.
- (6) Allcock, H. R. "Phosphorous-Nitrogen Compounds": Academic Press: New York, 1972, and refs. therein.
- (7) Austin, P. E.; Riding, G. H.; Allcock, H. R. Macromol. 1983, 16, 719.
- (8) ^{31}P NMR: -6.3 ppm ($\text{H}_3\text{PO}_4/\text{D}_2\text{O}$). Anal. Calcd. for $\text{PNC}_{10}\text{H}_{22}\text{O}_6$: P, 10.93; N, 4.94; C, 42.40; H, 7.83; O, 33.89. Found: P, 10.50; N, 5.00; C, 41.84; H, 7.73; O, 34.93 (diff.). $M_N > 10^6$.
- (9) Tasi, Y. T.; Whitmore, D. H. Solid State Ionics 1982, 7, 129.
- (10) Bauerle, J. E. J. Phys. Chem. Solids 1969, 30, 2657.
- (11) MacDonald, J. R. J. Chem. Phys. 1974, 61, 3977.
- (12) Dupon, R.; Papke, B. L.; Ratner, M. A.; Shriver, D. F. J. Electrochem. Soc. 1984, 131, 586.

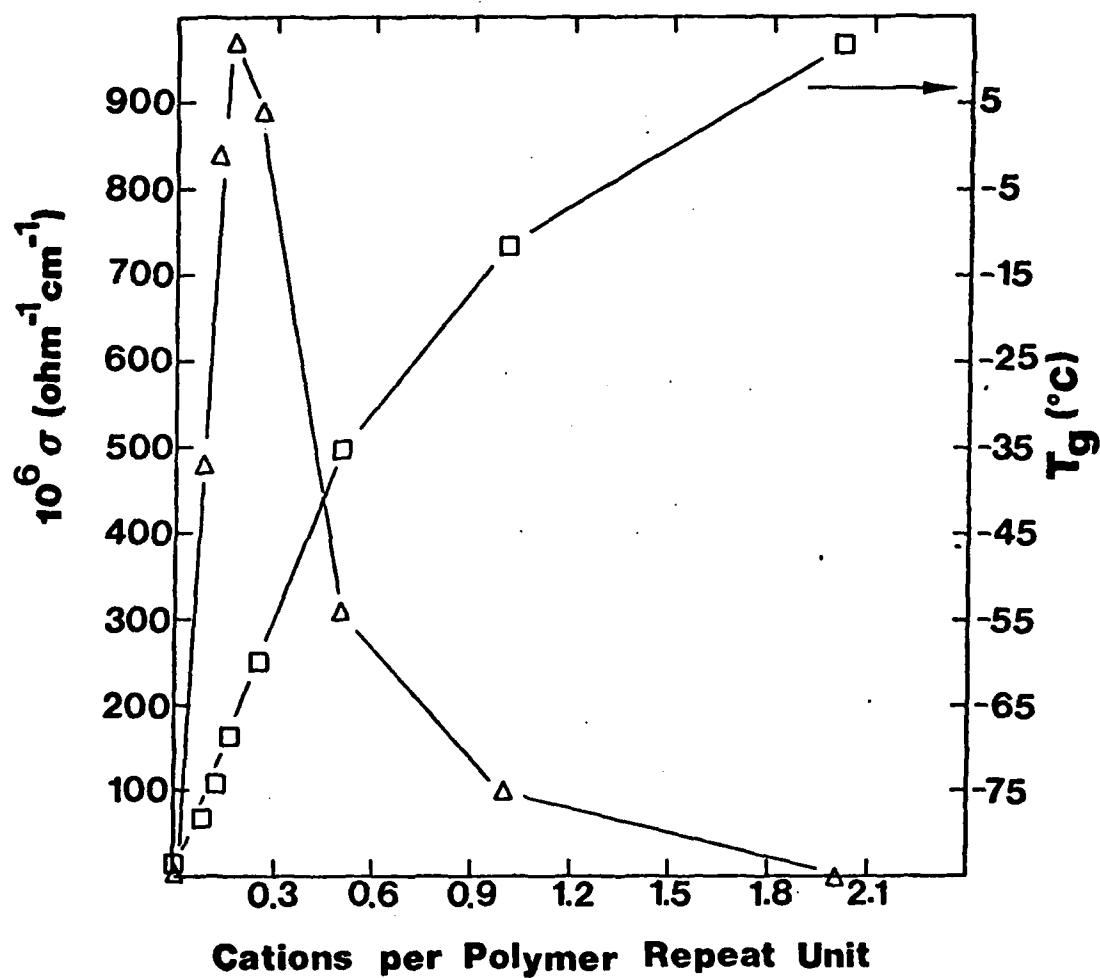
- (13) Papke, B. L.; Ratner, M. A.; Shriver, D. F. J. Electrochem. Soc. 1982, 129, 1694.
- (14) Cheradame, H. in "IUPAC Macromolecules": Benoit, H.; Rempp, P. eds., Pergamon Press: New York, 1982, 251.
- (15) Sorensen, P. R. Solid State Ionics 1983, 9&10, 1147.
- (16) Weston, J. E.; Steele, B. C. H. Solid State Ionics 1981, 2, 347.
- (17) Weston, J. E.; Steele, B. C. H. Solid State Ionics 1982, 7, 81.

Figure Captions

Figure 1. Temperature dependence of electrical conductivity, $\sigma(\text{ohm}^{-1}\text{cm}^{-1})$ plotted as $\ln(\sigma T^{1/2})$ vs. $1/T$. (Plots of $\ln \sigma$ vs. $1/T$ have the same qualitative shapes.) The wide error limits for the highest temperature point of the Sr- and Na-containing samples arise from flow of the samples and corresponding uncertainty in its thickness. $(\text{MSO}_3\text{CF}_3)_{0.25}\cdot\text{MEEP}$ complexes: Δ , pure polymer; +, Sr; Δ , Na; \square , Li; X, Ag.

Figure 2. Left axis: Δ , Electrical conductivity at 70°C vs. composition of $(\text{AgSO}_3\text{CF}_3)_x\cdot\text{MEEP}$ complexes. Right axis: \square , T_g (extrapolated to $0^\circ/\text{min}$ heating rate) vs. composition of $(\text{AgSO}_3\text{CF}_3)_x\cdot\text{MEEP}$ complexes.





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